

**THERMOCHEMICAL STUDIES
ON RARE EARTH DIGLYCOLATE
COMPLEXES**

By

HEIKKI OTS

LUND 1970

Rättelser

Del	Sida	Plats	Står	Skall stå
Samman- fattning	9	r 28	foramtion	formation
	16	r 15	effect	effects
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	1076	Tabell 6 Kolumn 4 <u>o</u> 6	$\Delta C_{p,w}^{\infty}$	$-\Delta C_{p,w}^{\infty}$
II	2	r 11	lanthanide	lanthanoid
	2	r 27	stabilit	stability
	3	r 13	T	The
	3	r 16	potentio	potentio-
	4	Höger halvcell	0.975 NaClO ₄	0.975 M NaClO ₄
III	1	r 16	became	become
	3	r 16	logk(T)	logK _i (T)
	10	r 23	logk f(T)	logK _i f(T)

THERMOCHEMICAL STUDIES ON RARE EARTH

DIGLYCOLATE COMPLEXES

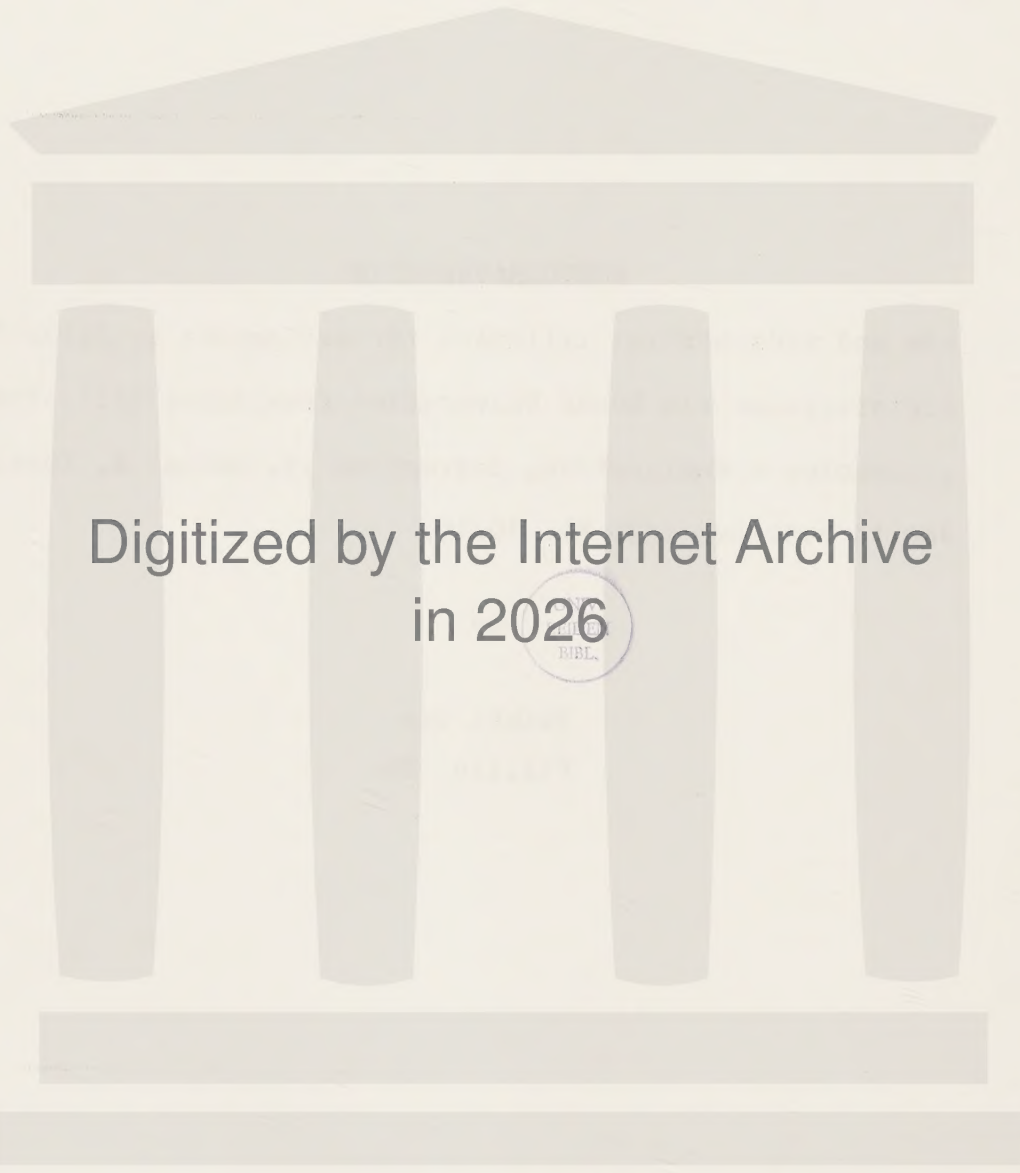
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Heikki Ots
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Avdelningen för fysikalisk kemi 1, Lunds Universitet,
Box 740, 220 07 Lund 7.



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DIGLYCOLATE COMPLEXES

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Heikki Ots

Lund 1970

The present review gives a summary of the results from the following papers. They will be referred to by their roman numerals.

I. Grenthe, I., Ots, H. and Ginstrup, O. A Calorimetric Determination of the Enthalpy of Ionization of Water and the Enthalpy of Protonation of THAM at 5, 20, 35, and 50 °C. Acta Chem. Scand. 24 (1970) 1067.

II. Ots, H. Thermochemical Studies on Rare Earth Diglycolate Complexes.

I. Stability Constants and Free Energy Changes at 5, 20, 35, and 50 °C.

III. Ots, H. Thermochemical Studies on Rare Earth Diglycolate Complexes.

II. Enthalpy and Heat Capacity Changes at 5, 20, 35, and 50 °C.

INTRODUCTION

Lanthanum and the succeeding 14 lanthanoids form the longest series of chemically similar elements in the periodic table. The normal valence of the lanthanoid ions is 3+ and the succeeding ions in the series successively add 14 electrons to the 4f sub-shell. The inner orbitals are rather effectively shielded from interactions with outer electrostatic fields by electrons in the 5s and 5p orbitals. The influence of the 4f electrons on the chemical properties is thus only of minor importance and ligand field effects are also much smaller for the rare earth ions than for d-type transition metal ions.

As the nuclear charge increases across the rare earth series, the electron shells are pulled closer to the nucleus. As a consequence, the ionic radius decreases as the atomic number increases and the field at the surface of the ion increases across the series. The influence of the decreasing ion size on hydration, coordination number and coordination geometry is a unifying concept in the coordination chemistry of the lanthanoid ions.

Coordination in the solid state. X-ray diffraction and other methods for structural determinations of crystals have shown that the normal coordination number for the lanthanoid ions is larger than $6^{1.6}$. In fact, the coordination numbers range in most cases from 6 to 9, but can be as high as 12 with ligands like nitrate and sulphate^{2,3}. Monodentate ligands, e.g. the halides, surrounding the lanthanoid ion form a coordination polyhedron based upon either a trigonal prism or an octahedron. Both polyhedra have 6-coordinated lanthanoid ions but the coordination may be expanded to 7, 8, or 9

e.g. by coordination of additional ligands through the square faces of the trigonal prism⁴. The bidentate and tridentate ligands normally form chelates with coordination numbers larger than 6¹.

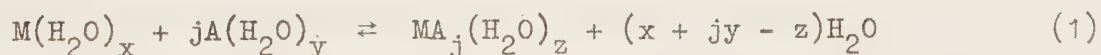
Crystal structure investigations of series of analogous compounds of Ln^{3+} -ions demonstrate the reduction in ion size as the 4f sub-shell is filled. For "open" structures such as the chelates this is usually shown as a decrease of the unit cell volume through the rare earth series. For some structures with monodentate ligands like e.g. the halide ions, the shrinkage of the rare earth ions has been demonstrated in a different way. When the size of the lanthanoid ion decreases, the repulsion between the ligands in the coordination sphere increases and becomes eventually large enough to make a structure with a smaller coordination more stable. The coordination number for the halide complexes thus decreases from 9 to 6 through the rare earth series.

Albertsson⁵ has determined the structures and the variation of the cell parameters of a series of lanthanoid diglycolate compounds by X-ray single crystal and powder techniques. The compounds had the general formula $\text{Na}_3[\text{M}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, $\text{M} = \text{Ce-Lu}$. The results obtained show that the structures were isomorphous. The coordination polyhedra were all described as distorted versions of the symmetrically tricapped trigonal prism (9 coordinated). The effect of shrinkage of the lanthanoid ions is thus, for these complexes, not demonstrated by a change of coordination number, but as a shrinkage and distortion of the coordination polyhedron. For the elements before Gd the decrease

in the unit cell volume is slightly less than the decrease in crystal radius of the lanthanoid ions. For the heaviest central ions a van der Waals contact is established between some of the coordinated oxygens resulting in a contraction of the unit cell appreciably smaller than the corresponding contraction of lanthanoid ions. The oxygen-oxygen contacts thus result in a hindrance for the formation of the third diglycolate complex in the latter part of the rare earth series.

Coordination in solution. The coordination chemistry in solution of the lanthanoid elements has been extensively studied^{1,6}. The very similar electron structure and the formation of mainly ionic compounds make the chemical properties of these elements very much alike. In aqueous solution they all form hydrated ions and complexes of the same type and of similar stability with a given ligand. There are, however, variations in the complex formation ability within the series, variations which in many cases may be attributed to the contraction of the metal ions.

The complex formation in solution can generally be written as (charges omitted):



where $M(H_2O)_x$ and $A(H_2O)_y$ are the hydrated forms of the metal ion and ligand, respectively. The mass action law for this reaction is often written as

$$\beta_j = \frac{[MA_j]}{[M] \cdot [A]^j} \quad (2)$$

where β_j is the over-all stability constant for the formation of the j :th complex.

The stoichiometric composition and the stability constants for the formation of a large number of complexes in solution have been determined^{1,6,8,10,11}. Such investigations are normally carried out by conventional methods, e.g. potentiometric, extraction and solubility measurements. Determinations of the enthalpy changes have also been made for some of these reactions. This has been done either by direct calorimetric measurements^{1,6,7,9} or from the temperature variation of the free energy changes^{1,6}.

The macroscopic thermodynamic properties, free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°), are related according to the equations:

$$\Delta G_j^\circ = -RT \ln \beta_j \quad (3)$$

$$\Delta G_j^\circ = \Delta H_j^\circ - T \cdot \Delta S_j^\circ \quad (4)$$

From these quantities additional information of the complex formation reactions is obtained. However, it is difficult to give a microscopic interpretation of macroscopic thermodynamic data in a system of strongly interacting particles. The molecular interpretations must thus be qualitative and are obtained by correlations between thermodynamic and non-thermodynamic data, e.g. kinetic¹²⁻¹⁴, spectroscopic¹⁵ or structural⁵. E.g. the thermodynamic investigations show for the carboxylate complexes that there is no monotonous variation of the thermodynamic quantities with ionic radius through the rare earth series. Furthermore, for the first complex formation step, very similar variations in ΔH_1° and ΔS_1° are obtained for different carboxylates as dipicolinate⁹, diglycolate⁹, acetate⁷ and EDTA¹⁶. (See also Ref. 17.) This indicates that a large part of the variation could be ascribed to some property of the metal ion.

Hydration, steric and ligand-field effects. The lanthanoid ions are hydrated in aqueous solution. The strong electrostatic field around the central ion produces a sphere of ordered structure of solvent molecules. The structure of this region is different from "normal" water and the spatial extent will be dependent on the radius and charge of the polarising ion^{18,19}. This sphere influences, via hydrogen bonds, the structure of the solvent cloud to some distance outside the first hydration sphere.

If changes in the geometric packing of the solvent molecules in contact with the metal ion were not to occur, we should expect the space of the cloud to vary in a regular way with the ionic radius. However, with decreasing ionic radius there is a possibility of such a change and this would influence the properties of the hydrated ions.

Exhaustive studies of the properties of the hydrated trivalent rare earths have been made by Spedding et al.²⁰. They studied variations of properties such as conductance, transference numbers, activity coefficients, heats of solution etc. for a number of rare earth salts. On the basis of these results they concluded that there is, owing to the lanthanoid contraction, a change in the effective hydration number of the lanthanoid ion somewhere in the middle of the series.

The variations of the thermodynamic quantities for various reactions in which complexes are formed are also seldom regular in the earth series and most often exhibit "breaks" in the middle of the series. This feature is common to a variety of reactions and the behaviour is suggested to reflect changes in the hydration of the rare earth ions. This model has been proposed by Grenthe¹⁷,

de la Praudiere²¹ and Choppin²². However, it is likely that in a series of partially hydrated complexes there is also some change in the number of water molecules occupying the vacant positions in the complex ions²³, but this need not necessarily take place at the same stage in the series as for the simple ions. Possibly then, the changes in the hydration for both the simple ions and their corresponding complexes contribute to the observed variations in the various thermodynamic quantities through the rare earth series.

Moeller et al.²⁴ have used these ideas on the formation of the rare earth tropolonato complexes. They have assumed the lack of irregular variation of ΔH_1^0 and ΔS_1^0 through the series to be caused by compensating hydration effects of the metal ions and their corresponding 1:1 complexes.

The ordered water structure around the metal ions can be interpreted as an entropy source. When the complexes are formed the structure is gradually broken down and this is accompanied by a positive entropy change. When succeeding ligands are coordinated the originally highly polarising metal ions are replaced by larger central groups with weaker fields and, consequently, the polarisation power is gradually decreased. We could thus expect the entropy changes for the stepwise reactions to decrease in the order $\Delta S_1^0 > \Delta S_2^0 > \Delta S_3^0$. This is also what is experimentally observed. Furthermore, the variations through the lanthanoid series of ΔH_3^0 and ΔS_3^0 for e.g. the diglycolate⁹ and dipicolinate⁹ complexes are much more regular than are the corresponding variations in ΔH_1^0 and ΔS_1^0 .

Other factors have also been suggested to be responsible for

the complicated behaviour of the thermodynamic quantities, e.g. ligand-field effects and steric hindrance. The latter effect is e.g. assumed to be responsible for the characteristic variations of the free energy changes, ΔG° , for the formation of the DTPA²⁵ and TPHA²⁶ complexes. For these complexes there is a steady increase in $-\Delta G^\circ$ from La(III) to Dy(III) which is in accordance with the decrease in ionic radius of the rare earth ions. At Dy(III) a maximum is reached and for the heavier rare earths there is a gradual decrease in $-\Delta G^\circ$. The decrease is assumed to reflect the increased difficulty for the very "bulky" DTPA and TPHA complexes to be formed in the latter part of the rare earth series. This effect is somewhat loosely described as "steric hindrance".

According to the observations of the lanthanoid diglycolate complexes, MA_3 , in the solid state, there is a hindrance for complex formation for the heavier rare earths in the series (page 2). In solution the trend observed for the variation in $-\Delta G_3^\circ$ for the formation of the third lanthanoid diglycolate complexes through the series⁹ is the same as for the above TPHA and DTPA complexes. However, for the diglycolate complexes, the presence of steric effects is strongly supported by the results from studies of the solid state⁵. Further evidence is also the rapid increase of the ratio $\frac{K_2}{K_3}$ between the second and third stepwise formation constants in the latter part of the rare earth series. This indicates the increasing difficulty for the third complex to be formed. The conclusion is further supported by the fact that a third diglycolate complex does not exist for the scandium ion²⁷.

These diglycolate complexes occur, in the solid state, as discrete units and it is very probable that they have about the

same structure in solution as in the solid state. The investigation of Larsen and Brown⁵⁴ on cerium(IV) ammonium nitrate revealed, that even a very high coordination number² is preserved in solution. It thus seems reasonable to compare solution data with those in the solid state.

The ligand-field effects have more or less been precluded from the discussion²¹, and the results from the study of Staveley et al.²⁵ do suggest only a minor degree of ligand-field stabilization (at most $200-400 \text{ cal}\cdot\text{mol}^{-1}$). The minor importance of this effect is consistent with the rather effective shielding of the 4f orbitals.

The evidence for hydration effects on the chemistry of lanthanoid ions in solution is generally indirect. However, the sum of information on lanthanoid ion coordination in solutions provides a high probability that the general model of decreasing coordination number with decreasing size is as definite and as important in solutions as in crystals. At the same time it is obvious from the above review that there are great difficulties in the interpretation of the thermodynamic measurements. Usually it is impossible to decide whether an observed change is caused by one or several of the species participating in the reaction. Interpretations of this kind would be facilitated if one could determine the partial molar contributions of the various species to the observed change.

The object of the present study. The aims of the present research on the rare earth diglycolate complexes in the temperature range $5-50^\circ\text{C}$ have been:

1. A determination of the temperature dependence of thermodynamic quantities ΔG_j° , ΔH_j° , and ΔS_j° for the stepwise reactions (II, III). The purpose has been to investigate whether the observed characteristic variations in the thermodynamic quantities through the

rare earth series are preserved in the temperature range.

2. A determination of the heat capacity changes, $\Delta C_{p,j}^0$, for the stepwise complex formation and the temperature dependence of this quantity (III). This determination, in combination with the partial molal heat capacities for the various rare earth perchlorates, makes it thus possible to determine the variation of the partial molal heat capacities for the various complexes through the lanthanoid series.

3. A comparison of the $\Delta G_j^0(T)$ -data obtained by direct potentiometric methods with those computed from $\Delta H(T)$ -data obtained from direct calorimetric measurements (II). The results from this comparison will thus direct future investigations on other complex systems, similar to those investigated here, so that the temperature dependences of the thermodynamic quantities can be obtained by the best and easiest way.

For the present investigation very accurate enthalpy data were needed and to accomplish this a new titration calorimeter was constructed (I).

The choice of ligand for the investigation was directed by several considerations. Firstly, the hydrogen diglycolate complexes are weak and can not influence the measurements. Secondly, only mononuclear complexes have to be considered and there is a well defined endpoint ($\bar{n} = 3$) for the complex formation. Finally, the ligand is easy to handle, behaves well in solution and the measurements are rather easy to perform.

The choice of this ligand leads, however, to one unfavourable situation. The stability constants β_1 for the rare earth complex formation are approximately two powers of ten greater than δ_1 and δ_2/δ_1 , the stepwise formation constants for the proton complexes.

For this reason the proton can not compete effectively with the metal ions for the ligand (see below) and the accuracy of $[A]$ becomes low at low values of $\bar{n}$ because $\underline{C}_H - [H^+] \ll \underline{C}_H$. This has been circumvented at the calculations by choice of the lower integration limit in a region where accurate $\bar{n} - [A]$ values can be determined (II).

EXPERIMENTAL PROCEDURE

The measurements have all been made in an aqueous sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M. This particular medium has been chosen in order to avoid correction for the heat of dilution of the sodium ion. Such corrections are large and could affect the accuracy of the calorimetric determinations. As a consequence, the perchlorate concentration varied slightly through a titration, but this did not influence the results, as indicated by both potentiometric and calorimetric experiments.

Determination of the stability constants. The equilibria in the praseodymium, samarium, dysprosium and ytterbium diglycolate systems have been investigated by means of a potentiometric method (II). In these systems the concentrations of free ligand or free metal ion can not be directly determined. For this reason a competition method has been used with the proton as a competitor i.e. the concentration of free ligand has been determined by means of $[H^+]$ -measurements. This has been done by measuring the emf of galvanic cells of the type:

Au	$\frac{C_M}{C_{H_2A}}$	lanthanide	1.00 M	0.025 M NaCl	Ag, AgCl
	$\frac{C_{H_2A}}{C_{Na_2A}}$	diglycolic acid	NaClO ₄	0.975 M NaClO ₄	
	$\frac{C_{Na_2A}}{(1.00 \text{ M} - \frac{v \cdot 2 \cdot C_{Na_2A}}{V_0 + v})}$	sodium diglycolate			
		1.00 M Na ⁺			
		Quinhydrone			

where $\underline{V}_0$ and $\underline{v}$ are the volumes of the solutions S and T, respectively.

The $[H^+]$ -concentration is given by the relation

$$\underline{E} = \underline{E}_0 + \frac{RT}{F} \ln[H^+] + \underline{E}_{\text{liq.junct.}} \quad (5)$$

where $\underline{E}_0$ is a constant provided that the ionic strength and temperature in the both half-cells are kept constant. During the experiments the temperature of the right half-cell was kept at 25.00 °C, while the titrations were performed in the left half-cell at 5.00, 20.00, 35.00, and 50.00 °C.

All the systems have been studied using the quinhydrone electrode as it seemed to have a better stability than the glass electrode, especially at higher temperatures. Most workers who have used the quinhydrone electrode have used solutions saturated with quinhydrone. However, the solubility of this compound increases rapidly with increasing temperature and saturated solutions can not be obtained, at say 50 °C, without fairly large changes of the composition of the solutions. For this reason a constant amount (0.001 g) of quinhydrone, has been used for all the titrations of the present work. This amount is small enough to dissolve completely at all temperatures investigated.

Determination of the enthalpy changes. The enthalpy changes for the complex formation reactions have been determined for the

praseodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, ytterbium and lutetium diglycolate systems (III). The direct calorimetric measurements have been performed, at 5.00, 20.00, 35.00, and 50.00 °C as titrations where small amounts of a solution T (disodium salt of the ligand) have been added to a solution S (rare earth perchlorate). The calorimeter used for these measurements was the isothermal jacket calorimeter constructed and tested at this laboratory (I).

Besides the conventional tests on accuracy and reproducibility of this calorimeter (see detailed description in part I), the enthalpy of ionization of water and the enthalpy of protonation of tris(hydroxymethyl)aminomethane, THAM, have also been determined at 5, 20, 35, and 50 °C (I).

The results obtained for the changes in heat capacity, $\Delta C_{p,w}^{\infty}$, for the ionization of water are in good agreement with those obtained by Ackermann and show a monotonous increase in the whole temperature range investigated with an expected maximum value at around 55 °-60 °C. This behaviour is not in accordance with the results obtained by Leung and Grunwald²⁹ who found a pronounced maximum at 35 °C. The difference between their investigation and ours seems to lie in the method used for extrapolation of the experimental heats of neutralization to infinite dilution. While Grunwald et al. have used the Debye-Hückel limiting law for apparent partial molal enthalpies for the corrections, we have used a combination of SVCTP-data and Ackermann's heat capacity data²⁸ (see I). Which of the two methods is the most reliable is hard to decide. One can only conclude that both methods are associated with errors and that these severely affect the final $\Delta C_{p,w}^{\infty}(T)$ -data. By experience (III) we do know that very small errors in the $\Delta H(T)$ -data can cause

substantial changes in the variation of the heat capacity change with temperature, and thus the establishment of the position of a maximum or minimum in the $\frac{\Delta C_p^0}{T}$ versus T curve is very difficult. A more definite answer can only be obtained by very time consuming measurements of the temperature dependence of the heats of dilution for the species involved.

CALCULATIONS

The stability constants (II). The stability constants for the various rare earth diglycolate systems have been calculated from the corresponding values of $\bar{n}$ and [A], obtained from the potentiometric measurements, by a least-squares program developed by Sillén and Ingri³⁰. For details see part II. The error limits used are three standard deviations.

The enthalpy changes (III). From the calorimetric determinations Q_{corr} -values were obtained (measured reaction heats corrected for the heats of dilution of ligand). These Q_{corr} -values, together with known stability constants β_i and δ_i and total concentrations, have been used for the calculations of the over-all enthalpy changes, ΔH_i^0 , for the various reactions. The calculations have been performed by use of the least-squares program "Letagrop Kalle" developed by Arnek³¹. For some of the systems β_i -values were known only at 20 °C. The values at the other temperatures were calculated as described in detail in part III. The error limits given for the enthalpy changes are one standard deviation.

RESULTS AND DISCUSSION

The variation of the thermodynamic quantities with temperature.

A feature in common for all the systems investigated is an increase in $-\Delta G_1^\circ$, ΔH_1° and $T \cdot \Delta S_1^\circ$ for the first complex formation steps with increasing temperature. As stated earlier¹⁷, the stability of the rare earth carboxylate complexes is due mostly to the large increase in entropy when the complex is formed. With increasing temperature this entropy stabilization is thus further pronounced.

The third complex formation step is different from the two previous one's in several respects. As mentioned before (page 6) hydration effects interfere to a much smaller extent here and the changes in the thermodynamic quantities are thus of different magnitudes than for the two previous reactions. In order to clarify the temperature variations for this reaction step it is suitable to divide the lanthanoid series into two parts.

For the first half of the series (Pr to Gd) there is an increase in $-\Delta G_3^\circ$ and a decrease in ΔH_3° with increasing temperature, while $T \cdot \Delta S_3^\circ$ is almost constant. The temperature effects on both the enthalpy and free energy changes are small compared with those for the two first reaction steps.

In the second half of the lanthanoid series (Tb to Lu) there is a decrease in all three thermodynamic quantities mentioned above. The temperature effect on $-\Delta G_3^\circ$ is, however, small. (For Lu $T \cdot \Delta S_3^\circ$ is constant.)

The entropy stabilization of the rare earth complex formation has been pointed out on several occasions. The entropy gained at each consecutive complex formation step decrease as a result of decreasing hydration. The sequence $\Delta S_1^\circ > \Delta S_2^\circ > \Delta S_3^\circ$ has been

observed not only for the rare earth carboxylate complexes, but for a variety of complexes with different central ions and ligand^{35,36}. The information obtained in this study on the rare earth diglycolate complexes reveals that the temperature derivatives of the stepwise entropy changes, $\frac{\delta(\Delta S_j^0)}{\delta T}$, decrease in the same order as the entropy changes themselves i.e.

$$\frac{\delta(\Delta S_1^0)}{\delta T} > \frac{\delta(\Delta S_2^0)}{\delta T} > \frac{\delta(\Delta S_3^0)}{\delta T} .$$

The thermodynamic quantities and their temperature derivatives can all be calculated by use of the results given in part II, Table 25 and part III, Table 8 and 10.

As discussed previously (page 7), the decrease in $-\Delta G_3^0$ in the latter part of the rare earth series was interpreted in terms of steric effects. When the temperature is increased there is, owing to the thermal agitation, a decrease in strength of the already previously weak bonding and, consequently, this must be reflected as a decrease in $-\Delta G_3^0$. This increased weakness of the bonding is clearly shown by the fact that the ratio $\frac{K_2}{K_3}$ for e.g. ytterbium diglycolate is almost 4 times as large at 50 °C as at 5 °C. Furthermore, when the temperature is increased, the steric effect (decreased $-\Delta G_3^0$) is established earlier in the rare earth series as seen from the variation of $-\Delta G_3^0$ with the ionic radius.

The heat capacity changes ΔC_{p1}^0 , ΔC_{p2}^0 and ΔC_{p3}^0 for the stepwise reactions are all temperature dependent, but the variation with temperature is not large. Minimum is obtained for all three quantities at around 30 °C, a feature in common with other systems³².

The occurrence of such minima for association reactions is, however, not restricted to this particular temperature range.

Minima have also been obtained at higher temperatures e.g. for the protonation of several carboxylates in aqueous solution the variations of the various heat capacity changes with temperature reach their minima at around 60° - 70°C ³³.

The reason for the occurrence of such minima is not clear, although it seems as the solvent somehow is involved.

The variation of the thermodynamic quantities with rare earth ionic radius. The variation patterns of $\underline{\Delta G_j^{\circ}}$, $\underline{\Delta H_j^{\circ}}$, and $\underline{\Delta S_j^{\circ}}$ for the stepwise formation of diglycolate complexes through the rare earth series have been interpreted in terms of variable hydration as discussed before (page 5). These characteristic patterns, obtained at 25°C , are on the whole unchanged in the temperature range investigated here. Thus, despite rather large changes in the three thermodynamic quantities with temperature, it seems as the effect responsible for the characteristic irregular variations through the rare earth series are substantially unaffected.

The temperature derivatives of the stepwise free energy and entropy changes are related to the corresponding entropy and heat capacity changes according to the equations:

$$\frac{\delta(\underline{\Delta G_j^{\circ}})}{\delta T} = -\underline{\Delta S_j^{\circ}} \quad (6)$$

$$\frac{\delta(\underline{\Delta S_j^{\circ}})}{\delta T} = \frac{\underline{\Delta C_{pj}^{\circ}}}{T} \quad (7)$$

The variation of these derivatives through the rare earth series is thus similar to the variation of the corresponding thermodynamic quantities $\underline{\Delta S^{\circ}}$ and $\underline{\Delta C_p^{\circ}}$.

The heat capacity changes, ΔC_{pi}° , for the stepwise reactions show unexpected variations through the rare earth series. In Fig. 2 part III such a variation is illustrated at 25 °C. The heat capacity changes are, as mentioned before (page 15), temperature dependent, but this does not influence the characteristic features of these variation plots.

The variation of ΔC_{p1}° (III, Fig.2) is the most regular one, with all values framed between 27 and 34 cal·mol⁻¹·K⁻¹. Still, three different regions can be discerned; two of approximate constancy at the beginning and in the end of the series and one of transition in between. The pattern is characteristic and similar to the variation of other thermodynamic (e.g. ΔS_1° for the rare earth diglycolates) and non-thermodynamic (e.g. rate constants for lanthanoid hydration¹³) quantities.

The variation plots of ΔC_{p2}° and ΔC_{p3}° (III Fig. 2) show quite different features. The maximum in ΔC_{p2}° and the minimum in ΔC_{p3}° , occurring in the region terbium-ytterbium, are unexpected. The difference between the ΔC_{p2}° and ΔC_{p3}° -values for the rare earths at the beginning and in the middle of the series is very large and amounts to 20 cal·mol⁻¹·K⁻¹. This implies that there must exist fundamental differences in the species participating in the reactions for the elements in the middle and at the beginning of the series. It is striking that the ΔC_{p2}° - and ΔC_{p3}° -curves are almost mirror images of each other which might indicate that it is the heat capacity of the second complex which is the origin of the observed variations.

Generally, the heat capacity changes decrease in the order $\Delta C_{p1}^{\circ} > \Delta C_{p2}^{\circ} > \Delta C_{p3}^{\circ}$. This, however, is not true for the elements

in the middle of the series for which ΔC_{p2}° is equal to or even larger than ΔC_{p1}° .

The observed variations in ΔC_{pj}° can not be quantitatively explained on the basis of the theoretical models presently available. If, however, the partial molal heat capacities for the species participating in the reactions are determined the interpretation of the variations would be much facilitated.

Such an investigation has recently been started at this laboratory and preliminary results are available, although only for two systems. The experimental procedure will be described very briefly here. A complete description will be given in a future communication.

The systems investigated so far are the praseodymium and holmium diglycolato systems. The measurements have been made at 25.00 °C by use of a specially designed calorimeter, which is a development of the titration calorimeter described earlier (I). The apparent molal heat capacities (ϕ_p) for the species $M(\text{ClO}_4)_3$, MClO_4 , NaClO_4 , and Na_2A have been determined in the concentration range 0.05 - 0.20 mol·Kg⁻¹, where an 1.000 mol·Kg⁻¹ sodium perchlorate solution has been regarded as the solvent. The plots of ϕ_p versus V_m gave straight lines from which the ϕ_p -value at $m = 0.020$ mol·Kg⁻¹ was extrapolated. This particular choice of concentration and solvent was made in order to make the results comparable with those obtained from enthalpy data (III). The partial molal heat capacities were then calculated by use of the relation:

$$\bar{C}_p = \phi_p + \frac{1}{2} V_m \frac{\delta \phi_p}{\delta (V_m)} \quad (8)$$

The results of the heat capacity measurements of the species in the praseodymium and holmium systems are given in Table 1. The first step of complex formation can be written as:



with the corresponding heat capacity change given as:

$$\frac{\Delta C}{p1}^0 = \bar{C}_{pMAClO_4} + 2\bar{C}_{pNaClO_4} - \bar{C}_{pM(ClO_4)_3} - \bar{C}_{pNa_2A} \quad (10)$$

Introduction of the values from Table 1 into relation (10) gives a remarkable agreement with the results obtained in part III Table 9. This is a confirmation of the reliability of the results obtained and the methods used.

The partial molal heat capacities for the second and third complexes in Table 1 have not been determined directly, but calculated from known values of $\frac{\Delta C}{p2}^0$ and $\frac{\Delta C}{p3}^0$ (part III Table 9).

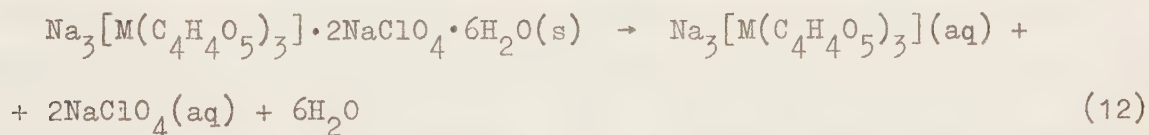
The material available so far is too small for any complete interpretation. There are, however, some interesting points worth making.

For praseodymium there is a rather regular increase in the partial molal heat capacities from the metal perchlorate to the third complex. This regular behaviour is not at all shown by the holmium complexes. The increase in the heat capacity from the metal perchlorate to the first complex is relatively small and is followed by a very large increase when the second complex is formed. The most notable point is, however, that the heat capacities for the second and the third complexes are equal. This is remarkable, as the third complex is formed simply by addition of Na_2A i.e.



and one would expect the heat capacity to increase. The conclusion which might first be drawn from these observations is that the heat capacity for the second holmium complex alone is exceptional, and thus responsible for the maximum and minimum obtained in the variation curves of $\frac{\Delta C}{p2}^{\circ}$ and $\frac{\Delta C}{p3}^{\circ}$ with the ionic radius. (Fig. 2 part III). Inspection of the results given in Table 1 indicates that a "normal" heat capacity value for the second complex should have been about $56 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. In that case both the maximum and minimum in the above curves would disappear. However, on the basis of preliminary data obtained on heats of solution, this reasoning turns out to be dubious.

We have lately started an investigation on the heats of solution for solid rare earth diglycolates i.e. the reaction studied is



This is thus the same compound for which the structure in the solid state has been determined earlier (see page 2).

The heat capacity change at 25°C for the above reaction shows the same trend through the rare earth series as the one obtained for the $\frac{\Delta C}{p3}^{\circ}$ variation in part III Fig. 2. This is obviously a further confirmation of the observed minimum in $\frac{\Delta C}{p3}^{\circ}$ in the middle of the lanthanoid series.

In the reaction above only the third diglycolate complex is involved, if we disregard water and sodium perchlorate, and the minimum in the $\frac{\Delta C}{p3}^{\circ}$ -curve is thus obtained without influence from any other species. Consequently, contrary to the discussion before, the second complex is not likely to be alone responsible for the observed minimum in the variation of $\frac{\Delta C}{p3}^{\circ}$ through the rare earth series.

According to these findings, the observed variations in the ΔC_{pj}° -values through the rare earth series are probably not caused by the variation of simply one species. On the contrary, this seems to be a combined effect of the variation of two species, one acting as product and the other as reactant in the complex formation reactions.

So far nothing has been said in this summary about the comparison of the $\Delta G_j^{\circ}(T)$ - and $\Delta H_j^{\circ}(T)$ -data obtained either by potentiometric or calorimetric determinations (see page 9). However, this has been discussed in full detail in part II and III and only some short remarks will be made here.

On the basis of the result obtained, it is clear that it is impossible to determine accurate enthalpy data from the temperature variation of the corresponding free energy changes. The potentiometric measurements are simply not accurate enough to permit such calculations. For strong complexes like the rare earth diglycolates the best and easiest way to determine all four thermodynamic quantities (ΔG_j° , ΔH_j° , ΔS_j° and ΔC_{pj}°) and their temperature dependences is a direct calorimetric determination of $\Delta H_j^{\circ}(T)$ -data combined with a potentiometric determination of ΔG_j° at one temperature. From these data $\Delta G_j^{\circ}(T)$, $\Delta S_j^{\circ}(T)$ and $\Delta C_{pj}^{\circ}(T)$ can be calculated. Accurate ΔC_{pj}° -values can only be obtained either from the temperature variation of the enthalpy changes or from direct determination of partial molal heat capacities.

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Table 1. The partial molal heat capacities for the various species participating in the formation of the praseodymium and holmium diglycolate complexes, at 25.00 °C and in 0.020 mol·kg⁻¹ solutions. An 1.00 mol·kg⁻¹ aqueous sodium perchlorate solution has been regarded as the solvent.

Metal Ion	$\frac{\bar{C}_P \text{ M(ClO}_4)_3}{\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{\bar{C}_P \text{ M(ClO}_4)_4}{\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{\bar{C}_P \text{ NaMA}_2}{\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{\bar{C}_P \text{ Na}_3\text{MA}_3}{\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{\bar{C}_P \text{ Na}_2\text{A}}{\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{\bar{C}_P \text{ NaClO}_4}{\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$
Pr	36.3	49.5	71.5	94.6	30.9	25.3
Ho	28.8	36.1	77.4	76.8		

